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THE EFFECTS OF MOLYBDENUM, TITANIUM AND NIOBIUM
ON THE HOT WORKING (CONTROLLED ROLLING)
BEHAVIOUR OF LINE-PIPE STEELS

Final Report

by

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EXECUTIVE SUMMARY

The effects of the microalloying additions Mo, Nb and Ti on delaying or preventing the recrystallization of austenite during controlled rolling are described. The rates of precipitation of NbCN and TiC at three different Mn levels are presented. The effect on roll force and torque of the presence of these elements in solution is also assessed. These data make it possible to predict the effects on steel rolling of substituting one or more of the microalloying additions by other combinations of these elements. The grain coarsening behaviour during the reheating of Ti and Nb microalloyed steels is compared, and the accelerated coarsening of NbCN precipitates under rolling conditions is also described.

RESUME

Le comportement d'aciers microalliés au Mo, Nb et Ti est étudié afin de déterminer dans quelle mesure ces microadditions retardent ou empêchent la recristallisation de l'austénite au cours du laminage contrôlé. Les vitesses de précipitation de NbCN et TiC sont mesurées et l'influence des différents éléments en solution sur les forces et couple de laminage est également calculée. Ces données permettent d'évaluer les différences obtenues au cours du laminage lorsqu'on remplace une ou plusieurs de ces additions par d'autres combinaisons de ces mêmes éléments. Les différents comportements d'aciers microalliés au Ti et Nb au cours du réchauffage en ce qui concerne le grossissement des grains sont comparés et le grossissement accéléré des précipités NbCN lors du laminage est également décrit.

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FINAL REPORT

The objectives of this project, as stated in the contract, were the following.

OVERALL OBJECTIVE:

On behalf of CANMET, Energy, Mines and Resources Canada, to conduct experimental research to determine the effects of the microalloying elements Mo, Nb and Ti on the rates of recrystallization, grain growth and precipitation in terms of controlled-rolling practice of high-strength line-pipe-grade steels, with a view to enabling reduction of microalloying costs and improvement of steel properties.

Sub-Objectives

1. To examine grain coarsening behaviour during initial reheat of the steels, and to choose a reheat treatment which will produce consistent, uniform starting grain sizes.
2. To determine the effects of Mo, Nb and Ti in solution on the retardation of dynamic recrystallization, and to relate these effects to roll separating forces in controlled rolling. Steels microalloyed with Mo, Nb and Ti, singly and in combination, are to be tested using hot compression and/or hot torsion methods.
3. To determine the precipitation kinetics of TiC , and the effects of the precipitation on dynamic and static recrystallization and grain growth in austenite.
4. To establish guidelines for composition and thermomechanical treatment of Ti-microalloyed steels in controlled-rolling practice.

PERSONNEL INVOLVED:

Professionals: Drs. M.G. Akben, T. Chandra, J.P. Michel and I. Weiss.

Students: H.L. de Andrade, B. Bacroix, T. Floros, W.J. Liu,
A. Macchione and P. Plassiard.

STAGES OF THE WORK:

The investigation was divided up into ten sub-projects, each of which provided a focus for the various working groups. The sub-projects are listed below, and the results obtained are summarized in turn.

1. Singly alloyed Nb and V steels (dynamic recrystallization and precipitation behaviour).
 2. Coarsening of Nb(CN) precipitates under rolling conditions.
 3. Effects of microalloying elements in solution on retardation of recrystallization.
 4. Controlled rolling behaviour of Mo microalloyed steels.
 5. Static recrystallization behaviour of Mo, Nb and V microalloyed steels.
 6. Effect of multiple microalloying additions on recrystallization and precipitation behaviour.
 7. Effect of Mn addition on the controlled rolling behaviour of Ti microalloyed steels.
 8. Solute hardening in Ti microalloyed steels.
 9. Effect of Ti concentration on the precipitation of TiC.
 10. Grain coarsening behaviour of Ti and Nb microalloyed steels.
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1. Effect of Nb and V Addition on Dynamic Recrystallization and Dynamic Precipitation in Microalloyed Steels

This work showed that increasing the Mn level in Nb steels from 0.42 to 1.9% shifts the C-curve for NbCN precipitation to the right by

more than an order of magnitude. The retardation in precipitation was attributed to the increase in carbonitride solubility caused by Mn addition, which was in turn linked with the decrease in the C activity associated with the presence of increased Mn. The high temperature solute strengthening produced by Mn, Nb and V addition was determined and the effect of this phenomenon on roll separating forces and torques was also predicted. It was shown that these effects are not solely dependent on atomic size differences, but that there is a significant contribution from the electronic differences between the solute elements as well. The details of this investigation were published in two parts: Ref. (1) in English and Ref. (2) in French.

2. Effect of Deformation and Recrystallization on the Coarsening of NbCN Precipitates

It is well known that carbonitride precipitates must be very fine ($< 100 \text{ \AA}$ in dia.) to be effective in preventing recrystallization and promoting pancaking during controlled rolling. Not as well understood is the effect of the rolling operation itself on the stability of these precipitates. What appears to occur is that rolling (deformation) causes very rapid coarsening of the carbonitrides to a size that renders them ineffective in preventing austenite recrystallization. For this reason, the temperature must be continuously decreased in controlled rolling so that fresh fine precipitates are deposited on the dislocation substructure. (This leads to problems in rod rolling, for example, a process in which there is considerable deformation heating.) In the investigation carried out at McGill, it was shown that the rate of dynamic and post dynamic coarsening (i.e. coarsening during and after deformation) was several orders of magnitude higher than during the classical (static) coarsening of undeformed materials. This was attributed to the dislocations introduced during straining and to the rapid solute transport occurring by pipe diffusion. It was shown that the rate of coarsening was higher at lower temperatures, contrary to expectation, because of the higher dislocation densities produced under these conditions. The accelerating effect of recrystallization, associated with the sweeping of the material by grain boundaries, was also determined. It was observed to increase the

rate of coarsening by a factor of about three with respect to the pipe diffusion case. The results of this sub-project were published in References (3) and (4).

3. Effect of Nb and V Addition When Present in Solute Form on Austenite Recrystallization

A controversy has long existed on the relative importance of solute vs. precipitate effects on promoting 'pancaking' during controlled rolling. This is partly because of the great effectiveness of additions of Nb and B, for example, at levels as low as 100 ppm atomic, which in turn seemed to be too low for the existence of plausible 'solute effects'. The relative merits of these two schools of thought were investigated thoroughly during the present contract period and the individual contributions of each of the two phenomena to the retardation of austenite recrystallization were delineated. It was shown that carbonitride precipitation, in general, was too slow to prevent austenite recrystallization on its own. This is because, in the absence of solute effects, recrystallization takes place in times of the order of 10 to 100 milliseconds in low alloy steels. The definitive experiments establishing the solute effect were carried out: (i) above the carbonitride solution temperature; (ii) in decarburized and denitrided steels; as well as (iii) at very short holding times. The relative importance and individual contributions of the two types of effect were reviewed in two publications; these are listed below as Refs. (5) and (6).

4. Controlled Rolling Behaviour of Mo Microalloyed Pipeline Steels

This project was carried out by B. Bacroix for her Master's thesis (Ref. 7); the results are discussed there in detail. In addition, parts of the work were published in the 1981 Pittsburgh conference on the 'Thermomechanical Processing of Microalloyed Austenite', Ref. (8). (This report was subsequently reprinted and given wide distribution by the Climax Molybdenum Company.) Further parts of the investigation were reported in Ref. (9) in English and in Ref. (10) in French. The results showed that the addition

of Mo to pipeline steels retards the precipitation of both NbCN and VN. This was attributed to the decrease in the activity coefficients of C and N caused by the presence of Mo in solution. The practical effect of this phenomenon is that Mo addition decreases the proportion of carbonitride precipitation in the austenite, but increases it in the ferrite. This change has two implications: (i) the increase in the proportion of ferrite precipitates leads to considerable strengthening because, being formed at lower temperatures, these are finer than the austenite precipitates; (ii) the decrease in the proportion of austenite precipitates does not reduce the pancaking temperature because the negative contribution of less austenite precipitation is more than overcome by the positive contribution of Mo addition in the form of the solute retardation of recrystallization. The solute retarding potential (SRP) of each microalloying element was also determined in this investigation (63, 10 and 3%, respectively, for Nb, Mo and V), as well as the influence of Mo addition on the γ -to- α transformation temperature when added to Nb and V steels. (It was shown that although Nb and V are γ stabilizers when added in normal microalloying amounts, they become α stabilizers in the presence of Mo in solution.) Thus, Mo-modified Nb-V steels can be finish rolled in the ($\alpha + \gamma$) phase field (which produces a component of substructure strengthening in the ferrite) at temperatures which are in the single phase γ region for the parent Nb-V steels.

5. Static Recrystallization Behaviour of Mo, Nb and V Microalloyed Steels

The singly alloyed steels in this series were tested by H.L. de Andrade and these results are described in detail in his Master's thesis (Ref. 11), copies of which have been made available to CANMET-PMRL. The multiply-alloyed steels were tested by T. Floros; his Master's thesis is under preparation and should become available in the summer of 1984 (Ref. 12.) There were two principal motivations for these two investigations. One is that the results described above concern the dynamic recrystallization behaviour of austenite and the associated dynamic precipitation kinetics. By contrast, under industrial rolling conditions, recrystallization and precipitation occur primarily under static (strain induced) conditions. Although static experiments are more difficult to carry out, and cannot in fact be used

when the recrystallization rate is either too fast or too slow, it was nevertheless necessary to carry out a kind of calibration between the more readily available dynamic observations and the trends to be expected under commercial static conditions. The second motivation concerned the desire to establish the kinds of softening (and precipitation) occurring in very short interpass times; e.g. times of the order of 50 to 100 ms. The results showed that V addition led to very little solute retardation of static recrystallization, and that Mo addition by contrast, led to considerably more retardation, whereas Nb addition led to the greatest retardation of all. These effects are observable at the shortest interruption times (e.g. 50 to 100 ms), and therefore prior to the onset of appreciable precipitation. An incidental aspect of this project concerned the effects of higher C levels, which reduced the amount of Nb that could be taken into solution (and therefore the extent of solute retardation), by reheating to a given temperature. Andrade's observations were published in Metall. Trans. as Ref. (13). Floros' results are to be presented at the forthcoming International Conference on High Strength Low Alloy Steels to be held in Wollongong, Australia in August 1984. (These will appear in the proceedings later in 1984, Ref. (14).)

6. Effect of the Combined Addition of Mo, Nb and V on the Recrystallization of Austenite

Under industrial rolling conditions, it is frequently observed that there are 'synergistic' effects involved in the use of multiple alloy additions. The dynamic test methods described above, however, while revealing synergistic strengthening effects, did not produce results supporting the existence of the synergistic solute retardation of recrystallization. One of the effects of carrying out the 'calibration' relating the dynamic to the static results was a resolution of this conflict. The static data clearly confirmed the existence of synergistic solute retardation and thus led to an overall synthesis of the test results which is clearly satisfactory. It is now well established that multiple additions of Mn, Mo, Nb, Ti and V, when present in solution, retard recovery and recrystallization to a greater

extent than can be estimated from the arithmetic sum of their individual effects. These additions also delay the process of carbonitride precipitation in austenite, leading to more precipitation in ferrite. Further to the activity changes described above, it appears that multiple alloying also decreases the diffusivities of the precipitating species. Finally, under multiple alloying conditions, the strengthening contribution of each element is greater than when it is added alone. A detailed report describing the above results was presented at the 1983 International Conference on the Technology and Applications of High Strength Low Alloy Steels in Philadelphia and has now appeared in the proceedings (Ref. 15). Further details of this work will be reported at the 1984 HSLA meeting in Wollongong, Australia as References (14) and (16).

7. Recrystallization and Precipitation Behaviour of Titanium Microalloyed Steels

Investigations of the Ti series of microalloyed steels were set up as four separate thesis projects, carried out by P. Plassiard (Ref. 17), W.J. Liu (1 - M.Eng. (18) and 1 - Ph.D. (19)) and A. Macchione (20). Liu's Master's thesis was funded in part by a contract with the Algoma Steel Corporation. Contributions to the Ti investigation were also made by Dr. T. Chandra (a visiting professor from Australia). Only one of the theses has been completed to date (Ref. 18); one has been abandoned for medical reasons (Ref. 17), and two are in progress, with completion expected in early 1985 (20) and early 1986 (19). Some of the work has been published in the international literature (Refs. 21 and 22), and two further papers will be available in late 1984 (Refs. 14 and 16.) The results obtained to date can be summarized as follows.

Effect of Mn Addition on Static and Dynamic Recrystallization.

When the Mn level was increased from 0.5 to 1.6 wt %, the dynamic RTT (recrystallization-time-temperature) curves were progressively shifted to longer times. This is attributed to the increased presence of Mn in solution, which appears to have two effects: (i) it increases the solubility

of TiC, thus decreasing the driving force for precipitation; (ii) it decreases the diffusivity of Ti. The former phenomenon probably involves the decrease in C activity associated with increasing the Mn concentration. The apparent decrease in Ti diffusivity in turn is probably also linked to the influence of Mn concentration, in a manner analogous to that reported for the Nb-Mn interaction (23). Thus there is considerable similarity between the effect of Mn addition on TiC precipitation on the one hand and on NbCN precipitation on the other. The experiments of A. Macchione on the same steels (20), which involve the influence of Mn addition on the static precipitation of TiC are not yet complete; the results obtained to date are consistent with the trends observed in the dynamic results which were summarized above.

8. Solute Hardening and Retardation of Recrystallization in Ti Microalloyed Steels

The increase in the yield strength of austenite associated with Ti addition was established as 42% per 0.1 wt % addition. This compares with strengthening contributions of 44, 25, 8, 5, 2 and 1% for equivalent additions of Nb, Al, V, Mo, Mn and Si (22). The strengthening contribution of each element (on a fixed atom fraction basis) was found to correlate very well with the respective size misfit parameter. This experimental quantity is based on the combined effects of atom size differences and electronic and modulus differences. The solute retardation of recrystallization produced by Ti addition was also assessed. The rank order observed (Nb, Ti, Al, V, Mo, Mn and Si) followed that determined for the strengthening contributions.

9. Effect of Ti Concentration on the Precipitation of TiC in Microalloyed Steels

A second series of Ti steels is currently being tested by W.J. Liu (19). These include Ti levels from 0.03 to 0.22% Ti, with a base composition involving 0.1% C, 1.5% Mn, 0.02% Al, 0.30% Si, 0.006% N, 0.008% S and 0.003% P. The effects of increasing Ti concentration on the TiC precipitation kinetics are being assessed; so are the influence of Ti in solution on

the flow stress of austenite and on the solute retardation of austenite recrystallization. If sufficient funding is obtained to continue the investigation, it is also intended to study:

- (i) the coarsening behaviour of TiC under industrial rolling conditions; and
- (ii) the relation between the isothermal and continuous cooling PTT curves for TiC precipitation.

These data are required to permit the design of controlled rolling schedules which are specific to the Ti steels. These schedules will have to take into account the differences between the effects of Ti and Nb in solution on the retardation of recrystallization, as well as the differences between the precipitation characteristics of TiC and NbCN.

10. Grain Coarsening Behaviour During Reheating of Ti and Nb Microalloyed Steels

Although not formally a part of this contract, two associated studies (carried out under contract to the Algoma Steel Corp.) helped us to attain the first sub-objective of the contract. The first investigation concerned (in part) the grain coarsening behaviour on reheating of a Nb and a Nb-V microalloyed steel. The results of this project were presented at an ASM Symposium and were published as Ref. 24. The second investigation concerned (in part) the grain coarsening behaviours of two Ti-modified steels (Ref. 25). When the results of these two independent studies are compared, the greater grain refining power of Ti addition is readily evident. In particular, it is to be noted that a 0.03% addition of Ti led to a reheated grain size of 140 μm at 1250°C; this was further reduced to 125 μm when the Ti level was increased to 0.10%. By contrast, the grain sizes of the two Nb steels (0.066% Nb and 0.046% Nb + 0.05% V) were 260 and 270 μm after reheating to 1250°C. Further work will be undertaken (given suitable financing) to extend the above two investigations, which should lead, on completion, to a report of practical interest.

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